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Permalink

<https://escholarship.org/uc/item/8g01j6z4>

Journal

Journal of the American Chemical Society, 130(52)

ISSN

0002-7863

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Publication Date

2008-12-01

DOI

10.1021/ja807126u

Peer reviewed

Synthesis, Characterization, and Theory of [9]-, [12]-, and [18]Cycloparaphenylene: Carbon Nanothoop Structures

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Due to their unique architectural features, the cycloparaphenylenes (**1**, Figure 1) have attracted attention from many vantage points.¹ Their strained and distorted aromatic systems and radially oriented p orbitals (**2**) have intrigued synthetic chemists, theoreticians, supramolecular chemists, and materials scientists alike. Despite this widespread interest, the cycloparaphenylenes remain an unsolved synthetic challenge.^{2–4} Here we describe the first synthesis of [9]-, [12]-, and [18]cycloparaphenylene. We also utilize computational methods to understand the structural and optical properties of these new macrocycles. As these structures correspond to the shortest-possible segment of an armchair carbon nanotube,⁵ we refer to them as “carbon nanothoops.”

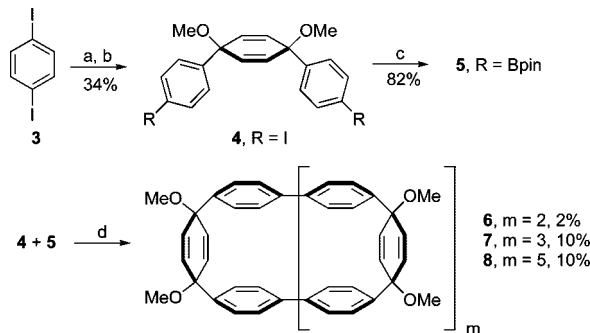
The heart of the synthetic challenge for the cycloparaphenylenes lies in the strain energy of the bent aromatic system.⁶ Our strategy was to build up strain sequentially during the synthesis, using a 3,6-*syn*-dimethoxy-cyclohexa-1,4-diene moiety as a masked aromatic ring in a macrocyclic intermediate (see structure **4**, Scheme 1). We reasoned that the cyclohexadiene unit would provide the curvature and rigidity necessary for macrocyclization to afford a marginally strained intermediate. Subsequent aromatization would then provide the driving force necessary to achieve the strain energies of target compounds, calculated to be 47, 28, and 5 kcal/mol for [9]-, [12]-, and [18]cycloparaphenylenes, respectively (*vide infra*).

The synthesis of the macrocyclic precursors to cycloparaphenylenes is depicted in Scheme 1. Monolithiation of diiodobenzene and subsequent addition of benzoquinone generated a *syn* diol,⁷ which was then alkylated with methyl iodide to produce diiodide **4** in an overall yield of 34%. In preparation for a tandem Suzuki coupling/macrocyclization sequence, portions of diiodide **4** were converted to diboronate **5** in a straightforward manner. Advantageously, both coupling partners could easily be prepared on a gram scale without the need for column chromatography. Standard Suzuki reaction conditions afforded macrocycles **6**, **7**, and **8** in 22% combined yield (Scheme 1). Formation of macrocycle **6** was unexpected and likely involves homocoupling of diboronate **5** as the intermediate step.⁸ Although the yield of macrocyclization products was modest, the synthetic route provided rapid access to three different macrocycles, which were easily separated by column chromatography. It is notable that the construction of macrocycle **8** involved formation of 18 carbon–carbon bonds in only 4 steps.

With the macrocyclic precursors in hand, we turned our attention to the aromatization reaction. To date, no efficient reactions to convert the cyclohexadiene moiety to a para-substituted aryl ring had been reported in the literature.⁹ Cyclohexadiene compounds similar to ours have been aromatized under acidic conditions, but only with concomi-



Figure 1. Cycloparaphenylenes (**1**) and a schematic of their radially oriented p orbitals (**2**).

Scheme 1. Preparation of Macrocyclic Precursors^a

^a Reagents and conditions: (a) (i) *n*BuLi, THF, -78°C , (ii) benzoquinone; (b) (i) NaH, THF, 0°C , (ii) MeI, 0°C to rt; (c) (i) *n*BuLi, THF, -78°C , (ii) isopropyl pinacol borate (Bpin), -78°C ; (d) Pd(PPh₃)₄, Cs₂CO₃, toluene/methanol (10:1), 80°C .

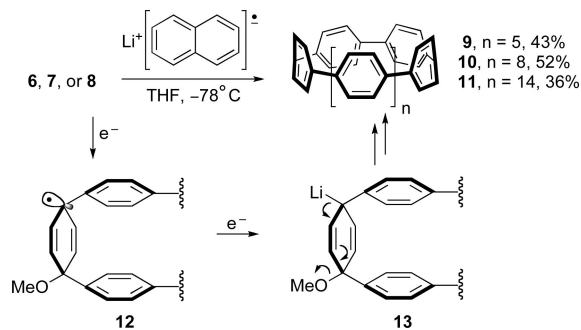


Figure 2. Aromatization reaction and proposed mechanism.

tant alkyl shifts generating 2,4-dialkylanisole derivatives.¹⁰ We attempted to circumvent such rearrangements with the use of strong nucleophilic hydride sources¹¹ but without success. Similarly, reducing conditions employing Stephen's reagent¹² or low-valent titanium¹³ led to complex mixtures due to the Lewis acidic nature of the reagents.

Lithium naphthalenide, a reagent known to reduce benzylic ethers at low temperature,¹⁴ provided the eventual solution (Figure 2). Treatment of each macrocycle (**6**, **7**, and **8**) with lithium naphthalenide at -78°C afforded the corresponding cycloparaphenylenes (**9**, **10**, and **11**) in moderate yields. Mechanistically, the reaction is envisioned to proceed via an initial one-electron transfer which generates stabilized radical intermediate **12** and an equivalent of lithium methoxide. A

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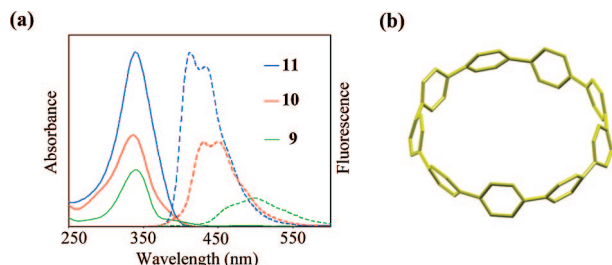


Figure 3. (a) Absorption (solid line) and fluorescence (dashed line) spectra of carbon nanohoops **9**, **10**, and **11**. (b) Energy-minimized geometry of carbon nanohoop **9** by DFT calculations.

second electron transfer then produces the alkyl lithium **13** which can aromatize via loss of a second equivalent of lithium methoxide. Especially noteworthy is the formation of cycloparaphenylene **9**, the most strained carbon nanohoop of the series, using these low-temperature conditions.

With cycloparaphenylenes in hand for the first time, we analyzed their properties using a variety of methods.¹⁵ Interestingly, their UV/visible absorption spectra showed symmetric peaks with a maximum at ~340 nm regardless of carbon nanohoop size (Figure 3a). Indeed, the smallest carbon nanohoop (**9**), which has the poorest geometry for orbital overlap and fewest number of aryl rings, has a slightly smaller optical absorption gap than that of the larger carbon nanohoops. This result stands in sharp contrast to the acyclic paraphenylenes in which a narrowing of the optical absorption gap occurs with extended conjugation.¹⁶ The fluorescence spectra also provided some unexpected results. As carbon nanohoop size decreased, the Stokes shift increased. Interestingly, the smallest carbon nanohoop **9** shows an especially broad spectrum with a large Stokes shift of approximately 160 nm.

We further investigated the structural and optical properties of the carbon nanohoop molecules with computational methods based on density functional theory (DFT).¹⁵ Our calculations indicate the favored geometry for the even-membered nanohoops, [12]- and [18]cycloparaphenylene, is a staggered configuration in which the dihedral angle between two adjacent phenyl rings alternates between 33° and 34°, respectively. This arrangement minimizes steric repulsion between neighboring aryl rings. For [9]cycloparaphenylene, the situation is slightly more complex. Reduced symmetry due to an odd number of phenyl rings results in a lowest energy conformation in which the dihedral angle varies between 18°, 30°, 31°, and 33° around the carbon nanohoop (Figure 3b).¹⁵ We found that chiral Möbius-strip like arrangements, where the dihedral angle is successively increased by ~35° around the ring, were higher in energy by at least 2 kcal/mol per phenyl ring. The calculated strain energies of carbon nanohoops **9**, **10**, and **11** were 47, 28, and 5 kcal/mol with diameters of 1.2, 1.7, and 2.4 nm, respectively.

We also performed DFT calculations to understand the counterintuitive trends in the observed optical data. We estimated the average optical absorption energy gap, E_g , with the following approximate formula: $E_g = \text{ionization potential (IP)} - \text{electron affinity (EA)} - E_{e-h}$, where E_{e-h} is the electron–hole interaction energy between the highest-occupied and lowest-unoccupied DFT one-electron wave functions.¹⁵ As expected, we observed that IP – EA decreases as the number of phenyl rings increase, in both the cyclic and acyclic cases. Remarkably, however, we found that the magnitude of E_{e-h} grows more dramatically with the decreasing number of phenyl rings for carbon nanohoops than for their acyclic counterparts.¹⁷ This computed trend in E_{e-h} more than compensates for the increase in IP – EA and results in an overall decrease in E_g with nanohoop diameter, in agreement with the experimentally observed trends. The fluorescence

data were also rationalized with DFT methods. The large Stokes shift observed in these spectra is governed by the degree of structural relaxation in the optically excited state. In the smaller nanohoops, enhanced curvature leads to greater sp^3 hybridization and increasingly asymmetric p orbitals, with their smaller lobes oriented inside the nanohoops. This factor reduces steric interactions and facilitates a larger decrease in dihedral angle in the excited state for the smaller nanohoop. Thus smaller hoops have the potential for larger structural relaxation and Stokes shifts. Indeed constrained DFT calculations confirmed the observed trend that the smallest carbon nanohoop has the largest relaxation in its excited state.¹⁵

In conclusion, we have demonstrated the first synthesis and characterization of [9]-, [12]-, and [18]cycloparaphenylene, the fundamental unit of an armchair carbon nanotube. It may be possible to prepare extended carbon nanotubes using similar solution phase chemistry without the need for high temperatures. Preparation of carbon nanotubes of a specific chirality⁵ utilizing these carbon nanohoop structures as templating agents is an intriguing prospect.

Acknowledgment. This work was performed at the Molecular Foundry. Experimental work was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. Theoretical work was supported by the National Science Foundation through the Network for Computational Nanotechnology, Grant EEC-0634750.

Supporting Information Available: Procedures for the synthesis and characterization of all new compounds and details of the computational analyses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA807126U